

## Relative Coordinating Abilities of Bis(pyridine)-Type Ligands When Forming Mixed-Ligand Coordination Polymers: Preparation and Structure of $[\text{Cd}_2(\text{L}^1)_2(\text{L}^2)(\text{NO}_3)_4]_\infty \{(n\text{-py})\text{-CH=N-C}_{10}\text{H}_6\text{-N=CH-}(n\text{-py}) [n = 3 (\text{L}^1), 4 (\text{L}^2)]\}$

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Porous materials have long been studied, and they are still one of the hot research topics in chemistry. Coordination polymers, one class of such materials, have many useful properties that can apply in a variety of fields, including catalysis, conductivity, luminescence, magnetism, adsorption-desorption, and gas storage.<sup>1-8</sup> They are prepared from various metals with suitable coordination spheres and a wide range of ligands with donor atoms in proper positions. In particular, the careful choice of linking ligands has proved to be critical to the preparation of desirable coordination polymers with cavities or channels.

For the past several years, our research group has prepared various coordination polymers, especially those based on *d*-block metals and bis(pyridine)-type ligands.<sup>9-18</sup> In particular, we recently examined the connecting modes of linking ligands containing different terminal groups (pyridyl-amine or pyridyl-pyridyl) and their cadmium coordination polymers.<sup>9,10</sup> As an extension of our ongoing study, we performed a comparison of coordinating abilities of ligands that coexist in the reaction mixture and compete with each other to coordinate to metals. The ligands used in this study are presented in Chart 1.

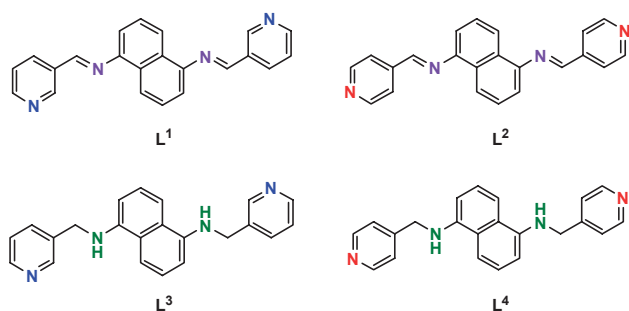
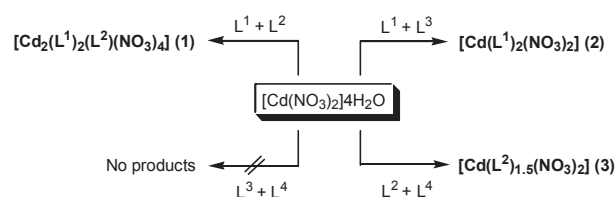


Chart 1

Our study has two main points. First, we investigated the coordinating abilities of a pair of ligands that have the same spacer (a central naphthalene diimine moiety) but different nitrogen-donor positions in terminal pyridyl groups: ( $\text{L}^1\text{-L}^2$ ) and ( $\text{L}^3\text{-L}^4$ ) pairs. Ligands  $\text{L}^1$  and  $\text{L}^2$  are structural isomers, and the same relationship also exists for the  $\text{L}^3\text{-L}^4$  pair. Second, we examined the effects of reduction on the coordination ability of ligands. For this study, we employed a pair of ligands con-



Scheme 1

sisting of a parent ligand and its corresponding reduced form: ( $\text{L}^1\text{-L}^3$ ) and ( $\text{L}^2\text{-L}^4$ ) pairs (Scheme 1). We report herein a comparison of coordinating abilities of four ligands  $\text{L}^1\text{-L}^4$  and a novel mixed-ligand coordination polymer of cadmium,  $[\text{Cd}_2(\text{L}^1)_2(\text{L}^2)(\text{NO}_3)_4]_\infty$  (1).

### Experimental Section

All solid chemicals were purified by recrystallization, and all solvents were distilled and stored over molecular sieves. Ligands  $\text{L}^1$  and  $\text{L}^2$  were prepared by the literature method.<sup>17</sup> Infrared (IR) samples were prepared as KBr pellets, and their spectra were obtained in the range 400 - 4000  $\text{cm}^{-1}$  on a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed by Analytical laboratory at Kangneung-Wonju National University.

**Preparation of (3-py)-CH<sub>2</sub>-NH-C<sub>10</sub>H<sub>6</sub>-NH-CH<sub>2</sub>-(3-py) ( $\text{L}^3$ ) and (4-py)-CH<sub>2</sub>-NH-C<sub>10</sub>H<sub>6</sub>-NH-CH<sub>2</sub>-(4-py) ( $\text{L}^4$ ).** Ligands  $\text{L}^3$  and  $\text{L}^4$  were prepared in the same way. A mixture of ligand  $\text{L}^1$  (0.50 g, 1.4 mmol) in methanol (50 mL) and sodium borohydride (0.52 g, 14 mmol) in dichloromethane (50 mL) was stirred for 12 h. The solvent was then removed completely, and the remaining solid was washed with deionized water (100 mL) and then extracted with dichloromethane (50 mL  $\times$  3). The dichloromethane solution was filtered with Celite and then concentrated to about one tenth of its initial volume. On addition of *n*-hexane (30 mL) to the concentrated solution, pale yellow powder was formed (210 mg, 0.6 mmol, 43% yield). mp 189 - 191 °C. Anal. Calc. for  $\text{C}_{22}\text{H}_{20}\text{N}_4$  ( $M_r = 340.17$ ): C, 77.62; H, 5.92; N, 16.46. Found: C, 76.86; H, 6.13; N, 16.02. <sup>1</sup>H-NMR ( $\text{CDCl}_3$ )  $\delta$  4.55 (d, 4H, N-CH<sub>2</sub>), 6.64 (t, 2H, NH), 7.06-7.79 (10 H, aromatic protons), 8.42 (d, 2H, pyridine NCH), 8.58 (s, 2H, pyridine N-CH). IR ( $\text{cm}^{-1}$ ): 3624 (m), 3265 (m), 2815 (w), 2623 (w),

2357 (m), 2071 (w), 1535 (s), 1427 (s), 1325 (w), 1098 (m), 923 (w), 767 (m).

**Data for L<sup>4</sup>:** Yield: 64%. mp 230 - 232 °C. Anal. Calc. for C<sub>22</sub>H<sub>20</sub>N<sub>4</sub> (*M<sub>r</sub>* = 340.17): C, 77.62; H, 5.92; N, 16.46. Found: C, 77.16; H, 6.19; N, 16.12. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 4.57 (d, 4 H, N-CH<sub>2</sub>), 6.50 (t, 2 H, NH), 6.81-7.51 (10 H, aromatic protons), 8.55 (d, 4H, pyridine N-CH). IR (cm<sup>-1</sup>): 3621 (w), 3552 (w), 3351 (m), 2844 (w), 2363 (w), 1932 (w), 1594 (s), 1539 (s), 1435 (s), 1328 (m), 1110 (m), 991 (m), 916 (w), 771 (s).

**Preparation of [Cd<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>(L<sup>2</sup>)(NO<sub>3</sub>)<sub>4</sub>]<sub>∞</sub> (1).** Ligands L<sup>1</sup> (68 mg, 0.2 mmol) and L<sup>2</sup> (33 mg, 0.1 mmol) were dissolved in tetrahydrofuran (13 mL, THF), and the resulting solution was filtered. An acetonitrile solution (3 mL, CH<sub>3</sub>CN) containing [Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O] (61 mg, 0.2 mmol) was prepared in the same way. The CH<sub>3</sub>CN solution was layered onto the top of the THF solution. The resulting solution was allowed to stand for 72 h to give brown crystals, which were filtered and then washed with ethanol (10 mL × 3) and dichloromethane (10 mL × 3) to give polymer **1** (108 mg, 0.146 mmol, 73% yield). mp 303 - 304 °C (decomp). Anal. Calc. for C<sub>33</sub>H<sub>24</sub>CdN<sub>8</sub>O<sub>6</sub>: C, 53.49; H,

3.26; N, 15.12. Found: C, 52.89; H, 3.40; N, 14.70. IR (cm<sup>-1</sup>): 2333 (m), 1619 (s), 1479 (s), 1290 (s), 1036 (m), 918 (m), 786 (s), 698 (m), 504 (s).

**Preparation of [Cd(L<sup>1</sup>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>∞</sub> (2) and [Cd(L<sup>2</sup>)<sub>1.5</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>∞</sub> (3).** Polymers **2** and **3** were prepared in the same way as polymer **1**. For the preparation of polymer **2**, L<sup>1</sup> (67 mg, 0.2 mmol), L<sup>3</sup> (68 mg, 0.2 mmol), and [Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O] (31 mg, 0.1 mmol) were used in the same amounts of solvents as those used for the preparation of polymer **1**. In preparing polymer **3**, L<sup>2</sup> (70 mg, 0.21 mmol), L<sup>4</sup> (71 mg, 0.21 mmol), and [Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O] (35 mg, 0.11 mmol) were used. Both polymers were brown crystals. Data for polymer **2**: 65 mg, 0.071 mmol, and 72% yield.

Data for polymer **3**: 70 mg, 0.094 mmol, and 85% yield.

**X-ray structure determination.** All X-ray data were collected on a Bruker Smart APEX2 diffractometer at the Cooperative Center for Research Facilities (CCRF) in the Sungkyunkwan University, which is equipped with a Mo X-ray tube. Absorption corrections were made by SADABS based on the Laue symmetry of equivalent reflections.<sup>19</sup> All calculations were carried out with SHELXTL programs.<sup>20</sup> The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in ideal positions and refined in a riding mode.

A brown crystal of polymer **1** of approximate dimensions 0.22 × 0.20 × 0.16 mm, shaped as a block, was used for crystal- and intensity-data collection. Details on crystal data, intensity collection, and refinement details are given in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC 773403 contains the supplementary crystallographic data for polymer **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

## Results and Discussion

**Preparation of ligands L<sup>3</sup> and L<sup>4</sup>.** In order to compare the coordinating abilities of a given ligand and its reduced form, we reduced the ligands L<sup>1</sup> and L<sup>2</sup>, which are structural isomers due to the different nitrogen positions in terminal pyridyl groups. When these ligands were treated with NaBH<sub>4</sub> in MeOH-CH<sub>2</sub>Cl<sub>2</sub>, the corresponding reduced forms (*m*-py)-CH<sub>2</sub>-NH-C<sub>10</sub>H<sub>6</sub>-NH-CH<sub>2</sub>-(*m*-py) [*m* = 3 (L<sup>3</sup>), 4 (L<sup>4</sup>)] were produced. Ligands L<sup>3</sup> and L<sup>4</sup> are also structural isomers. All four ligands may be regarded as relatively long bis(pyridine)-type linking ligands that possess an intervening naphthalene moiety and terminal pyridyls as coordinating groups. Whereas the π conjugation system in ligands L<sup>1</sup> and L<sup>2</sup> is complete, that in ligands L<sup>3</sup> and

**Table 1.** X-ray data collection and structure refinements

|   |   |
|---|---|
| Empirical formula                                 | C <sub>33</sub> H <sub>24</sub> CdN <sub>8</sub> O <sub>6</sub> |
| Formula weight                                    | 741.00  |
| Temperature, K                                    | 296(2)  |
| Crystal system                                    | triclinic   |
| Space group                                       | <i>P</i> -1   |
| <i>a</i> , Å                                      | 9.9875(4)   |
| <i>b</i> , Å                                      | 10.1139(4)  |
| <i>c</i> , Å                                      | 16.4811(6)  |
| <i>α</i> , deg                                    | 101.914(2)  |
| <i>β</i> , deg                                    | 107.027(2)  |
| <i>γ</i> , deg                                    | 94.352(2)   |
| <i>V</i> , Å <sup>3</sup>                         | 1540.9(1)   |
| <i>Z</i>  | 2   |
| <i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>     | 1.597   |
| <i>μ</i> , mm <sup>-1</sup>                       | 0.769   |
| <i>F</i> (000)                                    | 748   |
| <i>θ</i> range (°)                                | 2.08 - 28.42  |
| No. of reflections measured                       | 34539   |
| No. of reflections unique                         | 7547  |
| No. of reflections with <i>I</i> > 2σ( <i>I</i> ) | 3889  |
| No. of parameters refined                         | 433   |
| Max., in Δρ (e Å <sup>-3</sup> )                  | 0.540   |
| Min., in Δρ (e Å <sup>-3</sup> )                  | -0.540  |
| <i>GOF</i> on <i>F</i> <sup>2</sup>               | 0.951   |
| <i>R</i> <sub>1</sub> <sup>a</sup>                | 0.0517  |
| <i>wR</i> <sub>2</sub> <sup>b</sup>               | 0.0825  |

$${}^a R_1 = \sum[|F_o| - |F_c|]/\sum|F_o|, {}^b wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]^{1/2}$$

**Table 2.** Selected bond lengths (Å) and bond angles (°)

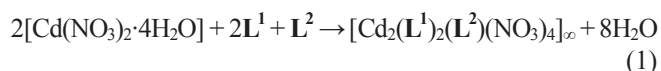
|             |          |              |          |           |          |
|-------------|----------|--------------|----------|-----------|----------|
| Cd1-N1      | 2.331(3) | Cd1-N5       | 2.363(3) | Cd1-O1    | 2.434(3) |
| Cd1-O4      | 2.460(3) | Cd1-O3       | 2.572(4) | Cd1-N4#1  | 2.363(3) |
| N2-C6       | 1.263(4) | N6-C26       | 1.253(4) |           |          |
| N1-Cd1-N4#1 | 86.6(1)  | N1-Cd1-N5    | 98.7(1)  | N1-Cd1-O1 | 86.8(1)  |
| N4#1-Cd1-N5 | 160.9(1) | Cd1-O4-Cd1#2 | 117.3(1) | Cd1-O4-N8 | 105.4(2) |

Symmetry transformations used to generate equivalent atoms: #1 = *x* - 1, *y* - 1, *z* - 1; #2 = -*x* + 1, -*y* + 1, -*z*.

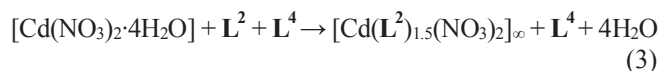
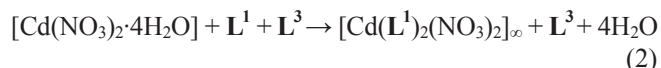
$L^4$  is disrupted by the  $-CH_2-NH-$  groups. Ligands  $L^3$  and  $L^4$  were characterized by  $^1H$  NMR, IR, and elemental analysis. The IR spectra of free ligands  $L^3$  and  $L^4$  display the N-H stretches at 3265 and 3351  $cm^{-1}$ , respectively.

**Comparative coordinating abilities of ligands.** For the systematic investigation of coordinating abilities of four ligands  $L^1$ - $L^4$  under competition conditions, we grouped the ligands into four pairs for a fixed metal complex:  $L^1$ - $L^2$ ,  $L^1$ - $L^3$ ,  $L^2$ - $L^4$ , and  $L^3$ - $L^4$ . When these four pairs were treated with  $[Cd(NO_3)_2 \cdot 4H_2O]$  under layer-diffusion conditions, three coordination polymers **1-3** were produced:  $[Cd_2(L^1)_2(L^2)(NO_3)_4]_\infty$  (**1**),  $[Cd(L^1)_2(NO_3)_2]_\infty$  (**2**), and  $[Cd(L^2)_{1.5}(NO_3)_2]_\infty$  (**3**). However, the reaction involving the  $L^3$ - $L^4$  pair gave no products (Scheme 1). Furthermore, reactions involving either  $L^3$  or  $L^4$  (in the absence of the partner) do not occur under the present reaction conditions. Polymers **1-3** are brown crystalline solids, and were structurally characterized by X-ray diffraction.

Polymer **1**,  $[Cd_2(L^1)_2(L^2)(NO_3)_4]_\infty$ , was obtained from the  $L^1$ - $L^2$  pair and  $[Cd(NO_3)_2 \cdot 4H_2O]$ , in which the mole ratio of  $L^1$ : $L^2$ : $[Cd]$  was 2:1:2 (eq 1). The 1:1:1 mole-ratio reaction also gave the same product in less than one half of the yield for the 2:1:2 mole-ratio reaction. These results indicate that the mole ratios of the starting compounds have no effects on the structure of the final product.



We also compared coordinating abilities of a parent ligand and its reduced form. For this study, the  $L^1$ - $L^3$  and  $L^2$ - $L^4$  pairs were treated with  $[Cd(NO_3)_2 \cdot 4H_2O]$  to give polymers **2** and **3**, respectively (eqs 2 and 3). The mole ratio among three components in each reaction was 1:1:1. X-ray crystallographic studies of polymers **2** and **3** revealed that these polymers are identical to the known coordination polymers  $[Cd(L^1)_2(NO_3)_2]_\infty$ <sup>11</sup> and  $[Cd(L^2)_{1.5}(NO_3)_2]_\infty$ ,<sup>17</sup> respectively, both of which were reported previously by our group. Polymer **2** was previously prepared from  $L^1$  and  $[Cd(NO_3)_2 \cdot 4H_2O]$  by layer diffusion (THF-MeOH). Polymer **3** was formed from  $L^2$  and  $[Cd(NO_3)_2 \cdot 4H_2O]$  also by layer diffusion (THF-EtOH). Although synthetic attempts in different solvent combinations were tried, the same products (polymers **2** and **3**) were always obtained in lower yields.



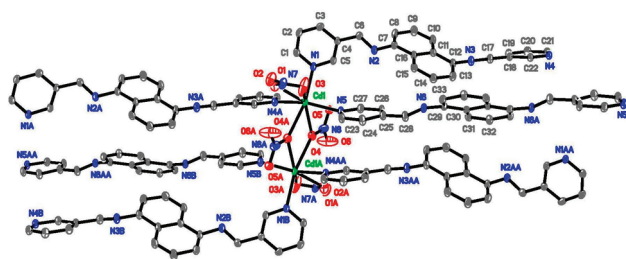
From the formation of polymers **1-3**, each of which was produced under competitive conditions between two components of a given ligand pair, several conclusions may be deduced. In polymer **1**, both  $L^1$  and  $L^2$  are coordinated to the Cd metals, so it would be difficult to distinguish their relative coordinating abilities. However, according to the mole ratio of these two ligands in the formula of polymer **1**, ligand  $L^1$  appears to have a better coordinating ability than ligand  $L^2$ . In polymers **2** and **3**, ligands  $L^3$  and  $L^4$  (reduced forms of ligands  $L^1$  and  $L^2$ ,

respectively) are not coordinated. Furthermore, as mentioned before, no products were obtained from the  $L^3$ - $L^4$  pair and  $[Cd(NO_3)_2 \cdot 4H_2O]$ . Consequently, ligands  $L^1$  and  $L^2$ , which have central imine ( $-CH=N-$ ) groups, appear to have much better coordinating ability than their reduced counterparts (ligands  $L^3$  and  $L^4$ ), which have the  $-CH_2-NH-$  groups. In fact, better coordinating ability of  $L^1$  and  $L^2$  in this study is inconsistent with our expectation. From the thermodynamic point of view, ligands  $L^1$  and  $L^2$  are expected to have lower coordinating abilities (or lower basicity) than ligands  $L^3$  and  $L^4$  (reduced forms), because the former ligands have a complete  $\pi$  conjugation system to which the nitrogen lone pairs in the terminal pyridyl groups may contribute and because they contain only saturated substituents. It should be mentioned that ligands  $L^1$  and  $L^2$  are more soluble than ligands  $L^3$  and  $L^4$  in our solvent combinations. Therefore, the above results probably tell us a well-known fact in crystal chemistry that coordinating ability (or ligand basicity) is a thermodynamic issue, but crystallization is a kinetic process.

**Structure of polymer 1.** Mixed-ligand coordination polymers have been prepared by employing two or more basically different linking ligands.<sup>21-24</sup> However, several polymers based on isomeric linking ligands recently appeared in the literature.<sup>25-28</sup> Such ligands are relatively short ones (bis(pyridine) or nicotinic acid) or bulky polyoxometalates, and therefore their coordination polymers of metals have rather small pores.

The local coordination environment around the Cd metals in polymer **1** are given in Figure 1, which demonstrates a dinuclear Cd core bridged by two  $NO_3$  ligands. An asymmetric unit consists of one Cd metal, two nitrate ligands, one  $L^1$  ligand, and one half  $L^2$  ligand. The Cd metal is coordinated to four oxygen atoms from three nitrate ligands and three nitrogen atoms from two  $L^1$  and one  $L^2$  ligands. This polymer has the  $[Cd_2(NO_3)_4]$  core as a knot (or a secondary building unit) with the Cd...Cd separation of 4.2190(6) Å. Four nitrate ligands behave differently: two of them as bidentate ligands ( $NO_3$ - $\kappa^2 O, O'$ ) and the other two as  $\mu_2$ -bridging ligands ( $\mu$ - $NO_3$ - $\kappa O$ ).

The packing diagram of polymer **1** along the  $a$ -axis is presented in Figure 2, which shows a complex 2-dimensional structure. Detailed linking patterns of ligands are depicted in Figure 3. The  $L^1$  ligands connect the  $[Cd_2(NO_3)_4]$  knots to form 1-D layers, which are further linked by  $L^2$  ligands to complete a 2-D structure (Figure 3a). It is worth noting that the largest pseudo-rectangular unit of polymer **1** can be taken by selecting four Cd metals, two  $L^1$ , and two  $L^2$  ligands (Figure 3b). The Cd...Cd separation linked by the  $L^1$  ligands is 17.1206(7) Å,



**Figure 1.** Local coordination environment of Cd in polymer **1**. Labeled atoms are related to non-labeled ones by the crystallographic inversion symmetry.

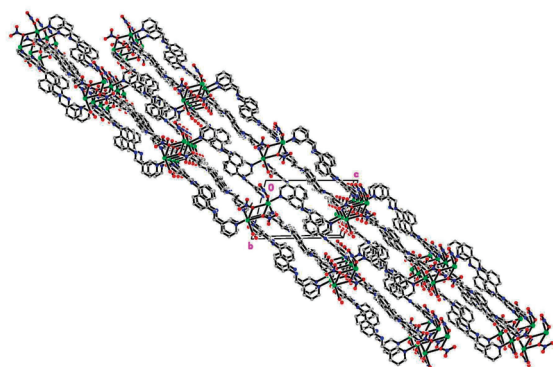


Figure 2. Packing diagram of polymer 1 along the *a*-axis.

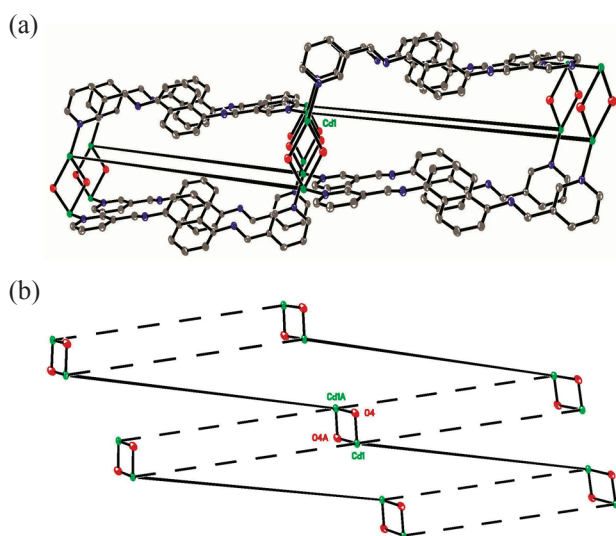


Figure 3. Linking patterns of ligands in polymer 1, in which the long lines denote  $L^2$  ligands and the  $[Cd_2(NO_3)_4]$  units are simplified into the  $[Cd_2O_2]$  units for clarity: (a) The  $L^1$  ligands connect the  $[Cd_2(NO_3)_4]$  knots (secondary building units) to form 1-D layers, which are further linked by  $L^2$  ligands to give a 2-D structure; (b) The schematic representation of Figure 3a in a different direction, in which the dotted lines correspond to  $L^1$  ligands. A larger pseudo-rectangular unit is formed by four Cd metals, two  $L^1$ , and two  $L^2$  ligands ( $17.12 \times 20.86 \text{ \AA}$ ), and a smaller one is formed by two  $L^1$  ligands and  $[Cd_2(NO_3)_4]$  units ( $17.12 \times 4.22 \text{ \AA}$ ).

and that by the  $L^2$  ligands is  $20.8590(10) \text{ \AA}$ . The difference in these separations originates in the difference in the nitrogen positions in the terminal pyridyls in these two ligands. The  $N1 \cdots N4$  separation ( $L^1$ ) is  $14.669(4) \text{ \AA}$ , and the  $N5 \cdots N5A$  ( $A = -x + 3, -y + 2, -z + 1$ ) separation ( $L^2$ ) is  $16.263(6) \text{ \AA}$ .

In summary, we investigated relative coordinating abilities of four bis(pyridine)-type ligands  $L^1$ - $L^4$ :  $L^1 = (3\text{-py})\text{-CH=N-C}_{10}\text{H}_6\text{-N=CH-(3-py)}$ ,  $L^2 = (4\text{-py})\text{-CH=N-C}_{10}\text{H}_6\text{-N=CH-(4-py)}$ ,  $L^3 = (3\text{-py})\text{-CH}_2\text{-NH-C}_{10}\text{H}_6\text{-NH-CH}_2\text{-(3-py)}$ , and  $L^4 = (4\text{-py})\text{-CH}_2\text{-NH-C}_{10}\text{H}_6\text{-NH-CH}_2\text{-(4-py)}$ . Ligands  $L^3$  and  $L^4$  were prepared by reducing  $L^1$  and  $L^2$ , respectively, with  $\text{NaBH}_4$  in  $\text{MeOH-CH}_2\text{Cl}_2$ . All four ligands are relatively long bis(pyridine)-type linking ligands that possess an intervening naphthalene moiety. Three pairs ( $L^1$ - $L^2$ ,  $L^1$ - $L^3$ , and  $L^2$ - $L^4$ ) reacted with  $[Cd(NO_3)_2 \cdot 4H_2O]$  to produce three coordination polymers,  $[Cd_2(L^1)_2(L^2)(NO_3)_4]$  (**1**),  $[Cd(L^1)_2(NO_3)_2]$  (**2**), and  $[Cd(L^2)_{1.5}(NO_3)_2]$  (**3**),

respectively. However, the reaction involving the  $L^3$ - $L^4$  pair did not occur. Polymer **1** is a rare example of mixed-ligand coordination polymers in which the linking ligands are structural isomers. Polymer **1** has a 2-D structure containing two pseudo-rectangles. The larger pseudo-rectangle is formed by four Cd metals, two  $L^1$ , and two  $L^2$  ligands ( $17.12 \times 20.86 \text{ \AA}$ ), and the smaller one is formed by two  $[Cd_2(NO_3)_4]$  units and two  $L^1$  ligands ( $4.22 \times 17.12 \text{ \AA}$ ). These experimental results strongly indicate that a kinetic factor is a dominating factor in determining the final product. In other words, the relative solubilities of two competing ligands are more important than the absence or presence of a  $\pi$  conjugation system in the competing ligands.

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